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Nanoscale Ionic Aggregates in Ionomer Melts

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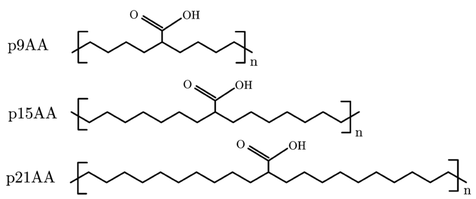
Abstract

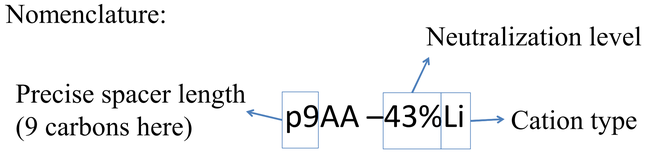
Designing acid- and ion-containing polymers for optimal proton, ion, or water transport would benefit profoundly from predictive models or theories that relate polymer structures with ionomer morphologies. Here, we present the first direct comparisons between scattering profiles, I(q), calculated from the atomistic MD simulations and experimental X-ray data for precise poly-(ethylene-co-acrylic acid) copolymer and ionomer melts. This set of precise polymers has spacers of exactly 9, 15, or 21 carbons between acid groups and has been partially neutralized with Li, Na, Cs, or Zn. The simulations reveal ionic aggregates with a range of morphologies, from compact, isolated aggregates (type 1) to branched, stringy aggregates (type 2) to branched, stringy aggregates that percolate through the simulation box (type 3). Excellent agreement is found between the simulated and experimental scattering peak positions across all polymer types and aggregate morphologies. This direct comparison of X-ray scattering data to the atomistic MD simulations is a substantive step toward providing a comprehensive, predictive model for ionomer morphology.

Introduction

- Nanoscale ion-rich aggregates form in ionomer melts
- Relationship between chemical structure and aggregate morphology poorly understood → **simulations of precise ionomer systems**
- PE backbone with precisely spaced COOH functional groups

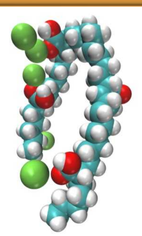


- Variations in spacer length, neutralization level and cation type
- Nomenclature:



MD Simulations

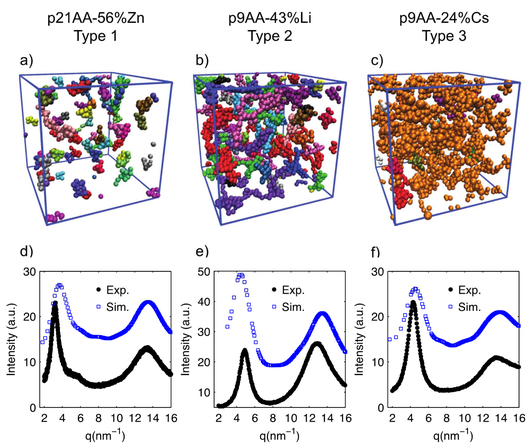
- 80-200 molecules, n = 4 repeat units
  → ~ 64 X 64 X 64 Å simulation box, total ~ 25,000 atoms
- LAMMPS used for MD production runs (~ 30 ns each), OPLS-AA fully atomistic force field



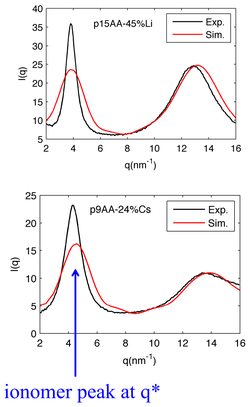
Fully atomistic representation of a single chain neutralized with Li^+

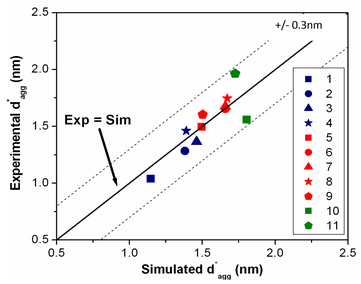
Scattering Data Compared to Simulations

Type I: isolated aggregates | Type 2: stringy aggregates | Type 3: percolated aggregates



direct comparisons:





compare ionomer peak locations

$$d^*_{agg} = 2\pi/q^*$$

p9 (p9AA, -43%Li, -33%Na, -24%Cs)

p15 (p15AA, -45%Li, -34%Na, -31%Cs, -82%Zn)

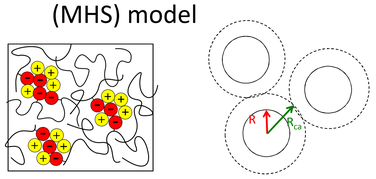
p21 (p21AA, -56%Zn)

Scattering Models

total scattering: $I(q) = I_{model}(q) + I_L(q) + C$

$I_{model}(q) = AP(q)S(q)$

Modified hard sphere (MHS) model

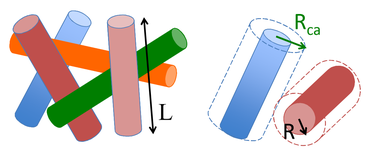


$I_{MHS}(q) = A\ (\Phi(qR))^2\ S_{HS}(q,R_{ca})$

sphere form factor | HS liquid structure factor

4 fitting parameters: A, ρ_{agg}, R, R_{ca}

New: Modified hard cylinder (MHC) model

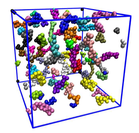


$I_{MHC}(q) = A\ P(qR,qL)\ S_{cyl}(q,R_{ca},L)$

cylinder form factor | HC liquid structure factor

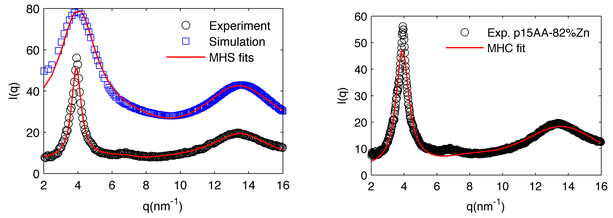
5 fitting parameters: A, ρ_{agg}, R, R_{ca}, L

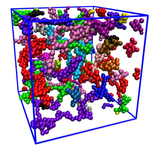
Morphology from Scattering Profiles?



for Type 1 discrete aggregates (p15AA-82%Zn)

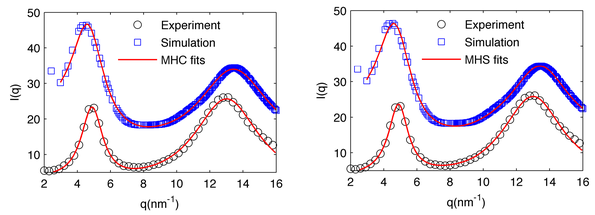
- MHS model fits better
- STEM indicates spherical aggregates





for Type 2 or Type 3 string aggregates (p9AA-43%Li)

- both models fit equally well
- R and R_{ca} are similar
- aggregates are composites of spherical and cylindrical parts



Conclusions and Future Work

- aggregates are often stringy
- percolated aggregates may enhance ion conductivity
- good agreement between simulation and experiment for structure factors
- cannot determine morphology from scattering alone

Future Work: compare dynamics between MD simulation and quasi-elastic neutron scattering (QENS)

Buitrago et al., *Macromolecules* 48, 1210-1220 (2015)
CINT User: Prof. Karen Winey, University of Pennsylvania

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